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THE STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF GRAPHENE OXIDE-BASED COUNTER ELECTRODE

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ABSTRACT

The graphene oxide (GO) -based counter electrode (CE) was fabricated on the fluorine-doped tin oxide (FTO) substrate. The GO and reduced GO (rGO) assisted by single-tail sodium dodecyl sulphate (SDS) and triple-tail sodium 1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-silphonate (TC14) surfactants were developed as CE material. The GO was synthesized by using an electrochemical exfoliation method. The synthesized GO was then reduced by using reduction process and hydrazine hydrate was used as reducing agent. The structural properties of TC14-rGO presented better properties as compared to the TC14-GO and SDS-rGO. Higher surface area and thinner layers of TC14-rGO demonstrated faster electron movement in the CE as compared to the low surface area. The TC14-rGO showed the lower optical transmittance value of 92.8% thanSDS-rGO of 97.4%. Higher electrical properties were also presented by TC14-rGO of 5.6 x 10-1 S. cm-1. Lower transmittance and higher electrical properties indicated lower oxygen content and thin layer of the TC14-rGO sample. Therefore, the TC14-rGO presented suitable to be applied as CE for dye sensitized solar cells (DSSCs) application.

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Introduction

In the recent years, the graphene oxide (GO) got an intensive attention for counter electrode (CE) material due to its good structural properties[1]. The GO structures are assumed as carbons which are covalently bonded on a homogeneous of sp2 graphitic basal plane[2]. The GO can be synthesized by using chemical vapor deposition (CVD) [3], Hummers method[4] and electrochemical exfoliation [5]. The CVD method included in physical approach, this method was rarely used due to its high temperature during the synthesis process. The Hummers method also presented high chemical consumption during the GO production, so this method included as an expensive method [4]. Therefore, the electrochemical exfoliation was chosen to the synthesis of GO. This method showed a simple method, low cost production and environmentally friendly[1, 6]

Actually, the GO can be synthesized in the acidic or shulphuric electrolytes. However, water-based electrolyte was chosen in the GO synthesis using electrochemical exfoliation method due to greener, safe and cheaper than another electrolytes [1]. In water-based electrolyte, the electrochemical exfoliation method needed a surfactant to help intercalate exfoliation and stabilize the exfoliated GO dispersion. The commercially available single-tail sodium dodecyl sulphate (SDS) [5]was commonly utilized to assist the GO synthesis in the electrochemical exfoliation method. However, the custom-made triple-tail sodium 1,4-bis (neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-silphonate (TC14) surfactants [1]was developed in this study in order to increase the stabilization of synthesized GO dispersion.

The synthesized GO showed high oxygen functional groupsthat indicated thick structure and low electrical properties [1]. Therefore, high oxygen functional groups in the synthesized GO was then reduced by using reduction process, this process can produce reduced GO (rGO). In this reduction process, the hydrazine hydrate was used as reducing agent due to its effectiveness in the reducing of GO content[7]. The thin films of synthesized GO and produced rGO were then fabricated by using the spray coating method. This method presented low cost, fast and simple to fabricate highly conductive film. The structuralproperties of TC14-GO, TC14-rGO and SDS-rGOthin films were characterized by using field emission scanning microscopy (FESEM), energy dispersive X-ray (EDX) and micro-Raman spectroscopy. The Ultraviolet,

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Visible (UV-Vis) spectroscopy and four-point probe measurement was used to determine the optical and electrical properties of samples, respectively. From the all analysis, the TC14-rGOthin film shows the best sample to be applied as CE for DSSCs application.

Materials And Method

The fabrication of GO-based CE thin film involved 3 steps. (1) First, the GO was synthesized by using electrochemical exfoliation method. This method used two pieces of graphite rods (99,99%, Good Fellow Company, Germany) and 7V was applied to 24hoursat room temperature during the GO synthesis process. The SDS and TC14 surfactants were used to assist the GO synthesis in order to help the exfoliation process in a water-based electrolyte. (2). Second, the synthesized GO was then reduced by using reduction process. Hydrazine hydrate was used as reducing agent in this process and the ratio of GO and hydrazine hydrate was 100:1. The reduction process was carried out for 24 hours at 95^{o}C. (3). Third, the synthesized GO and produced rGO were then transferred on the fluorine-doped tin oxide (FTO) substrate by using the spray coating method. Afterward, the sprayed TC14-GO, TC14-rGO and SDS-rGO were annealed in arGOn ambient at 400^{o}C for 1 hour. The fabricated TC14-GO, TC14-rGO and SDS-rGO thin films were then characterized by using FESEM-Hitachi Su8020, EDX-Horiba EMAX, micro-Raman spectroscopy (RenishawInVia micro-Raman System), UV-Vis spectroscopy (Agilent Cary60) and four-point probe measurement (Keithley 2636A).

Result And Discussion

The FESEM images of TC14-GO show thick layer and high agglomerated structure as presented in Fig 1 (a). This was believed due to high oxygen (O) content in the TC14-GO produced during the synthesis process by using an electrochemical exfoliation method. High O content was also confirmed by EDX analysis that the atomic % of O content shows a higher percentage of 58.97% as compared to the carbon (C) content of 27.85% (Fig. 1 (b)). The atomic % of Sn of 13.17% can be also detected in the TC14-GO thin film, which presents the composition of FTO substrate.

Fig. 1 (c) demonstrates the thinner layer of TC14-rGO in the edges as compared to the TC14-GO. Lower atomic % of O content in the TC14-rGO indicates to the thin layer of TC14-rGO sample as shown in Fig. 1 (d). The low O content of TC14-rGO was believed due to

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successfully reduction process by using hydrazine hydrate as reducing agent. The atomic % of O content decreases from 58.97% of TC14-GO to 39.98% of TC14-rGO. The SDS-rGOclearly presents thicker layer than TC14-rGO as demonstrated in Fig. 1 (e). This was believed due to single tail SDS surfactant used during the oxidation process. Single tail SDS surfactant shows lower exfoliation rate and stabilizationof produced GO as compared to the triple-tail TC14 surfactant [1]. This can be also proven by EDX analysis (Fig. 1(f)) that the atomic % of C content of 48.17% in the SDS-rGO is lower than C content in TC14-rGO of 49.32%.

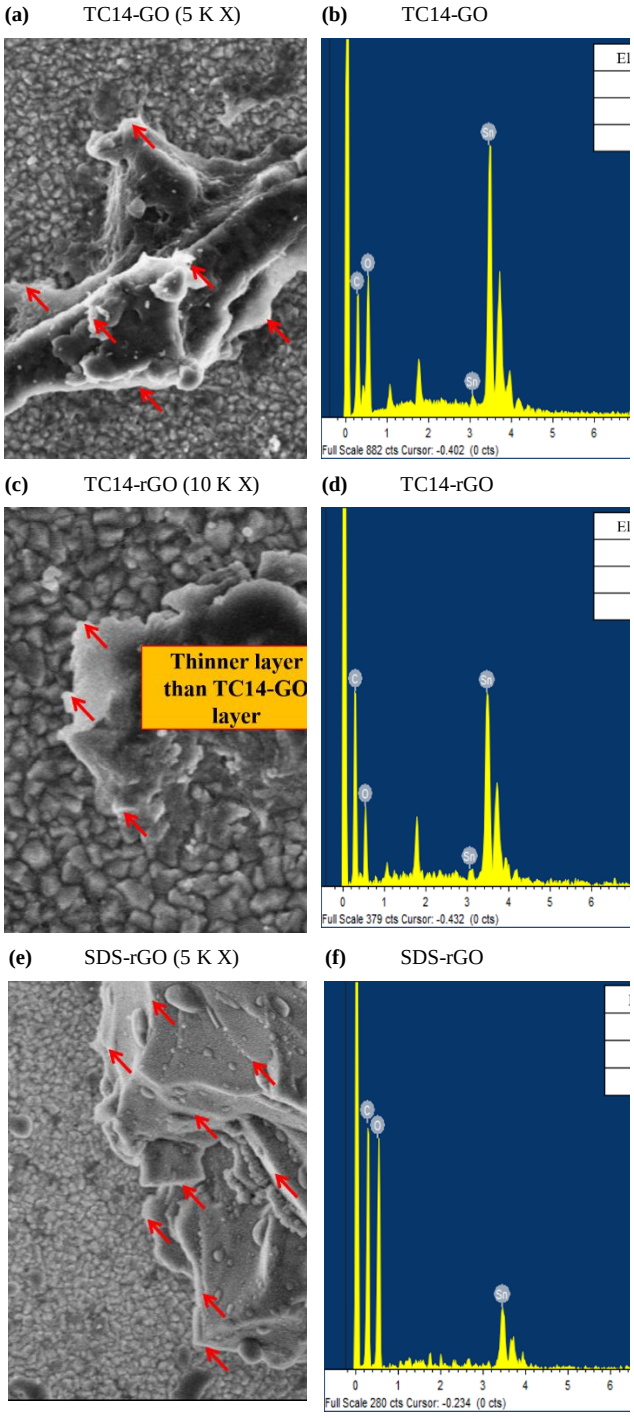

Fig. 1. FESEM images with EDX analysis of (a)-(b) TC14-GO, (c)-(d)TC14-rGO and (e)-(f)SDS-rGO.

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The micro-Raman spectra of TC14-GO, TC14-rGO and SDS-rGO are shown in Fig.2 which was used to analyze the crystallinity of samples. The D- and G-band can be clearly observed in the micro-Raman spectra of TC14-GO, TC14-rGO and SDS-rGO. The D- and G-band peak of TC14-GO are presented at 1348 and 1581 cm-1, respectively. The defect of carbon lattice in the sample can be obtained by D-band peak[8]. The G-bandpeakof TC14-GO demonstrates the exfoliated sheet layers synthesized using electrochemical exfoliation method[9]. After the TC14-GO was reduced into TC14-rGO, the TC14-rGO presents the D-band (1354 cm-1) and G-band (1585 cm-1)peakwhich shifted from D- and G-bandpeakof TC14-GO. This was believed due to reducing oxygen functional group during the reduction process. The D- and G-band peak of SDS-rGO are at 1360 and 1582 cm-1, respectively.

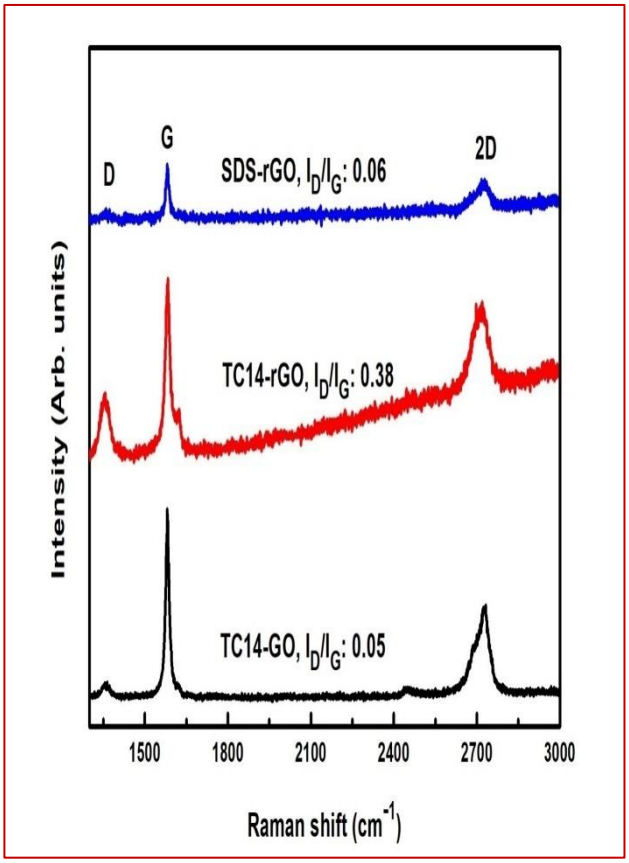

Fig. 2. Micro-Raman spectra of TC14-GO, TC14-rGOand SDS-rGO.

From the D- and G-band peak, the ID/IG ratio can be calculated. The existence defects of carbon samples can be determined by value of ID/IG ratio. The highest ID/IG ratio is shown by TC14-rGO of 0.38 which indicated the distortion of graphitic domains and reducing oxygen functional group in the reduction process (samadpour 2016). The SDS-rGO also demonstrated higher ID/IG ratio of 0.06 as compared to TC14-GO of 0.05. Higher ID/IG ratio of rGO samples than GO was believed

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due to utilization of hydrazine hydrate during the rGO production. Low ID/IG ratio of TC14-GO shows lower defect and amorphous carbon structure (Hessein 2016). From the micro-Raman spectra, the TC14-GO, TC14-rGO and SDS-rGO samples also present the 2D-band peak at 2720, 2725 and 2720 cm-1, respectively. The 2D-band peak in the samples revealed the number of GO and rGO layers (low 2013). The summary of micro-Raman analysis of TC14-GO, TC14-rGO and SDS-rGO are shown in Table 1.

Table 1 Summary of micro-raman analysis of TC14-GO, TC14-rGO and SDS-rGOthin films

Sample	D-peak (cm^{-1})	G-peak (cm^{-1})	I_D/I_G ratio	2D-peak (cm^{-1})
TC14-GO	1348	1581	0.05	2720
TC14-rGO	1354	1585	0.38	2725
SDS-rGO	1360	1582	0.06	2720

Fig.3 presents the UV-Vis spectra of TC14-GO, TC14-rGO and SDS-rGO. From this figure, the TC14-GO presents higher transmittance of ~99.3% as compared to the TC14-rGO of ~92.8% in the range of 400-800 nm at λ=550 nm[10]. Higher transmittance of TC14-GO was believed due to high oxygen functional group resulted during the electrochemical exfoliation method. The UV-Vis spectra also demonstrates that the TC14-rGO shows lower transmittance of ~92.8% than SDS-rGO of ~97.43% due to successfully reduction process of TC14-rGO.

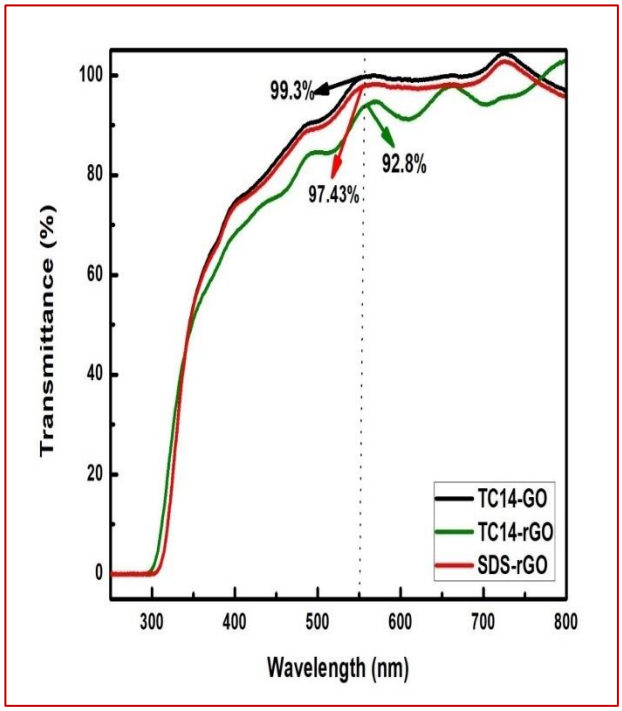

Fig. 3. Transmittancespectra of TC14-GO, TC14-rGO and SDS-rGO thin films

The electrical properties of TC14-GO, TC14-rGO and SDS-rGO can be determined by using four-point probe analysis as shown by I-V curves in Fig. 4. Based on the I-V curves, the TC14-rGO presents higher electrical conductivity of

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~5.6 x 10^{-1} S.cm^{-1} as compared to TC14-GO of ~4.3 x 10^{-1} and SDS-rGO of ~5 x 10^{-1} S.cm^{-1}.Lower oxygen functional group, less agglomeration and thin layer of TC14-rGO (see fesem image in Fig.1(c)) indicated higher electrical conductivity. The SDS-rGO shows lower electrical conductivity than TC14-rGO due to thicker layer and high agglomeration structure which indicated the slowness of electron movement in the sample during the four-point probe measurement.

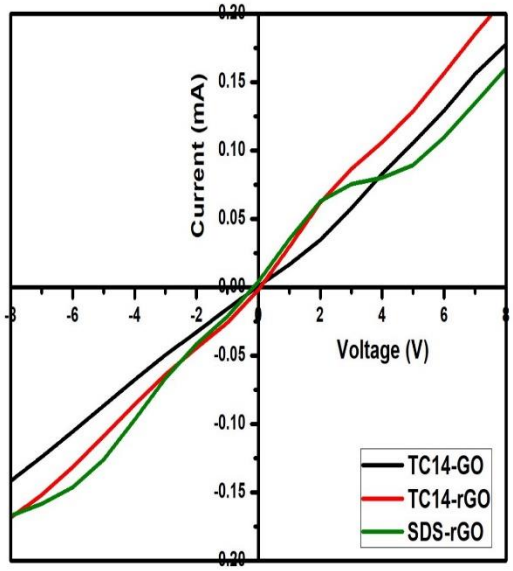

Figure 4. I-V curves of TC14-GO, TC14-rGO and SDS-rGOthin films

Conclusion

The TC14-GO, TC14-rGO and SDS-rGO were successfully fabricated as CE thin films for future DSSCs application. The structural properties of samples, thin film had been investigated by using FESEM, EDX and micro-Raman spectroscopy. The TC14-rGO showed the thinner layer and less agglomeration than SDS-rGO. This indicated successfully reducing oxygen functional group through the reduction process. Based on the micro-Raman spectra, the TC14-rGO also presented higher ID/IG ratio of 0.38 than SDS-rGO of 0.06. The optical and electrical properties of TC14-rGO demonstrated transmittance of ~92.8% and electrical conductivity of ~5.6 x 10-1 S. cm-1. Therefore, the TC14-rGO showed better structural, optical and electrical properties than other samples and indicated that the TC14-rGO thin film suitable to be applied as CE sample to DSSCs application.

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